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COORDINATION COMPOUNDS

Dioxomolybdenum(VI) Complexes with R1-Substituted Salicylidene Allylimines (Hl^n): Synthesis and Structure. Crystal Structure of $[MoO_2(L^1)_2]$ (R^1 = H)

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Abstract—The synthesis and X-ray diffraction analysis of $[MoO_2(L^1)_2]$ has been performed. The molybdenum atom has a *cis*(O_{oxo}), *cis*(N_L), *trans*(O_L) octahedral coordination. The average bond lengths (Å): Mo—O(oxo), 1.691; Mo—N(L^1), 2.351; Mo—O(L^1), 1.954.

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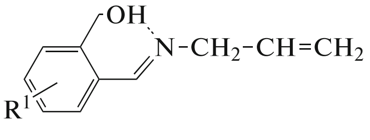
The benzoid–quinodal (keto–enol) tautometrism of salicylidene imines (*o*-oxyazomethines) opens opportunities for their use in the synthesis of complexes of various types and various structures with Lewis acids MX_m, such as adducts or molecular complexes containing neutral ligand molecules and chelates or intracomplex compounds, whose ligands are coordinated to the central atom in the form of deprotonated anions. The crucial role in the synthesis of molecular complexes or intracomplex compounds is played by the characters of the solvent and the salt anion [1]. For oxo- and dioxocations of VIB Group elements, including dioxomolybdenum(VI), complexes of both types predominantly with salicylidene aryl- and hetaryl amines have been synthesized and studied [2–4]. Much less attention has been paid to complexes with derivatives of substituted salicylic aldehydes and alkyl amines [5–7].

In this work, the synthesis of dioxomolybdenum(VI) molecular complexes and intracomplex compounds with salicylidene allylimines (HL^n) and the study of their properties were performed to continue the investigation of conditions for the synthesis of complexes of different types and gain more information about the structure of complexes with Group VIB element dioxocations (Scheme 1).



HL^n: R^1 = H (n = 1); 3-OMe (n = 2); 5-Br (n = 3); 3,5-Br_2 (n = 4); 3-OMe-5-Br (n = 5); 5,6-*cyclo*-C_4H_9 (n = 6)
Scheme 1.

The intracomplex compound $[MoO_2(L^1)_2]$ (**I**) was structurally characterized by X-ray diffraction.

EXPERIMENTAL

Synthesis. Salicylidene allylimines are readily formed upon the condensation of corresponding substituted salicylic aldehydes and allylamine in ethanol. Low-melting yellow crystalline compounds are obtained after exposure of azomethine solutions at 0°C for 24 h. Non-substituted salicylidene imine HL^1 representing a liquid at room temperature was purified by vacuum distillation. The purity of azomethines was controlled chromatographically and by the data of IR spectra.

Molecular complexes $MoO_2Cl_2 \cdot 2HL^n$ were synthesized by the immediate reaction between MoO_2Cl_2 and *o*-oxyazomethines in absolute diethyl ether. To a solution of MoO_2Cl_2 (0.199 g, 0.001 mol) in diethyl ether (10 mL), a solution of the corresponding azomethine (0.002 mol) in the same solvent was added drop by drop under stirring on a magnetic agitator. The reaction mixture was stirred for 20 min at room temperature. The formed precipitate was separated out on a porous glass filter equipped with a drying system filled with freshly calcinated calcium chloride, washed with ether, and dried on a filter in a dry argon flow.

Intracomplex compounds $MoO_2(L^n_2)$ are generally synthesized by two methods: ligand exchange between molybdenyl acetylacetonate and *o*-oxyazomethine and template synthesis [5]. It has been experimentally established that the second method is more preferable, as the complexes are produced in the form of crystal-

Table 1. Crystallographic data and selected characteristics of X-ray diffraction experiment for the structure of complex **I**

Formula weight	448.34
Color, habit	Light-yellow, acicular
Crystal size, mm	0.18 × 0.06 × 0.05
Symmetry system, space group	Monoclinic, $P2_1/c$
Unit cell parameters:	
a, Å	10.784(1)
b, Å	12.313(1)
c, Å	15.627(1)
β, deg	109.80(1)
V, Å^3	1952.2(3)
Z	4
ρ_{exp}, g/cm^3	1.518
μ_{Mo}, mm^{-1}	5.737
F(000)	904
T, K	293(2)
Radiation (λ, Å)	CuK_α (1.54178), graphite monochromator
Scanning type	ω
θ range, deg	4.36–64.95
Index ranges	$-1 \leq h \leq 12$, $-14 \leq k \leq 14$, $-18 \leq l \leq 15$
Total number of reflections/ independent reflections	6821/3205 [R(int) = 0.0217]
Completeness to θ = 64.95°	96.2%
Number of reflections with $I \geq 2\sigma(I)$	2716
Absorption correction	Semiempirical by equivalents
T_{min}/T_{max}	0.4252/0.7626
Number of refined parameters	245
GOOF on F^2	1.156
R [$I \geq 2\sigma$ (I)]	$R1 = 0.0440$, $wR2 = 0.1282$
R [all data]	$R1 = 0.0545$, $wR2 = 0.1372$
Extinction coefficient	0.0010(2)
Residual electron density (max/min), e/Å^3	0.493/–1.159

line powders with a good yield. To a suspension of molybdenyl salicylaldehydate MoO_2Sal_2 (0.740 g, 0.002 mol) in methanol (10 mL), allylamine (0.228 g, 0.3 mL, 0.004 mol) was added, and the reaction mixture was stirred at room temperature until the suspension was completely dissolved. The formed solution of the complex was allowed to stand in a cooler for 24 h for crystallization, and the crystals were separated out on a filter, washed with cold methanol, and dried first on a filter in a dry argon flow and then in a vacuum desiccator over $CaCl_2$.

Analysis for molybdenum was performed by calcinating a sample of the complex at 450°C until the formation of the MoO_3 gravimetric form [8]. Chloride was determined by the Volhard method after preliminary hydrolysis of a complex with an alkali solution [4]. The nitrogen content was estimated by the Dumas method [9].

IR spectra were recorded on an IKS-29 spectrometer as Nujol mulls.

X-ray diffraction analysis. The experimental material for a crystal of complex **I** was obtained on an Enraf-Nonius CAD-4 automatic diffractometer. The structure was solved by direct methods (SHELXS-86) [10] and refined by the least-squares technique in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [11]. The positions of hydrogen atoms were calculated geometrically and included into refinement as "riding." Unit cell parameters and selected characteristics of X-ray diffraction experiment are given in Table 1, and bond lengths and bond angles are listed in Table 2. Full crystallographic data were deposited with the Cambridge Structure Database (no. 1558124; http://www.ccdc.cam.ac.uk/deposit/).

RESULTS AND DISCUSSION

According to elemental analysis, the reaction between MoO_2Cl_2 and salicylidene allylimines gives adducts of the only composition $MoO_2Cl_2 \cdot 2HL^n$ (Table 3) representing amorphous hygroscopic powders, which are colored from yellow to orange-red, meltable at low temperatures, and soluble in polar solvents with their lightening in color due to the processes of solvolysis and the liberation of inner-sphere ligands.

In contrast to the molecular complexes, the synthesized intracomplex compounds represent fine-grained crystalline yellow or orange substances, which are non-hygroscopic, soluble in hot methanol, dimethylformamide, and dimethyl sulfoxide, and having higher melting points than in similar molecular complexes (Table 3).

Some information about the type of formed complexes and the location of the coordination bond between the metal and *o*-oxyazomethine may be obtained by studying the IR spectra of these compounds in the region 1700–1600 cm^{-1}. The observed high-frequency band at 1620–1630 cm^{-1} in the IR spectra of non-coordinated azomethines is assigned to the stretching vibrations of the C=N azomethine group [12]. This band is shifted towards lower frequencies at 8–10 cm^{-1} in the average upon the formation of intracomplex compounds, thus pointing to the participation of nitrogen from the C=N group in the donor–acceptor interaction with molybdenum with closure of the six-membered chelate ring $MoOC_3N$.

The IR spectra of the molecular complexes are observed to contain an intensive band in the same region at ~1650–1660 cm^{-1}, but its assignment

Table 2. Bond lengths (*d*) and bond angles (ω) in the structure of complex **I**

Bond	*d*, Å	Bond	*d*, Å
Mo(1)–O(2)	1.685(3)	C(3)–C(4)	1.397(6)
Mo(1)–O(1)	1.697(3)	C(4)–C(5)	1.376(6)
Mo(1)–O(4)	1.945(3)	C(5)–C(6)	1.386(7)
Mo(1)–O(3)	1.962(3)	C(6)–C(7)	1.353(7)
Mo(1)–N(2)	2.343(3)	C(8)–C(9)	1.514(7)
Mo(1)–N(1)	2.378(4)	C(9)–C(10)	1.278(9)
O(3)–C(3)	1.345(4)	C(11)–C(12)	1.448(6)
O(4)–C(17)	1.344(5)	C(12)–C(17)	1.397(6)
N(1)–C(1)	1.279(6)	C(12)–C(13)	1.403(5)
N(1)–C(8)	1.473(6)	C(13)–C(14)	1.370(7)
N(2)–C(11)	1.283(5)	C(14)–C(15)	1.366(7)
N(2)–C(18)	1.474(5)	C(15)–C(16)	1.379(7)
C(1)–C(2)	1.457(6)	C(16)–C(17)	1.397(6)
C(2)–C(3)	1.394(5)	C(18)–C(19)	1.494(6)
C(2)–C(7)	1.404(6)	C(19)–C(20)	1.282(6)
Angle	ω, deg	Angle	ω, deg
O(2)Mo(1)O(1)	107.28(18)	C(3)C(2)C(1)	123.0(4)
O(2)Mo(1)O(4)	96.36(13)	C(7)C(2)C(1)	118.3(4)
O(1)Mo(1)O(4)	98.63(15)	O(3)C(3)C(2)	122.2(3)
O(2)Mo(1)O(3)	95.13(13)	O(3)C(3)C(4)	118.2(4)
O(1)Mo(1)O(3)	95.51(13)	C(2)C(3)C(4)	119.5(4)
O(4)Mo(1)O(3)	158.23(15)	C(5)C(4)C(3)	120.0(4)
O(2)Mo(1)N(2)	163.81(16)	C(4)C(5)C(6)	120.6(4)
O(1)Mo(1)N(2)	88.87(14)	C(7)C(6)C(5)	119.8(4)
O(4)Mo(1)N(2)	79.70(12)	C(6)C(7)C(2)	121.4(4)
O(3)Mo(1)N(2)	84.13(12)	N(1)C(8)C(9)	109.1(4)
O(2)Mo(1)N(1)	86.88(16)	C(10)C(9)C(8)	124.9(8)
O(1)Mo(1)N(1)	165.29(15)	N(2)C(11)C(12)	125.9(4)
O(4)Mo(1)N(1)	83.31(13)	C(17)C(12)C(13)	118.6(4)
O(3)Mo(1)N(1)	78.91(11)	C(17)C(12)C(11)	123.4(4)
N(2)Mo(1)N(1)	77.08(12)	C(13)C(12)C(11)	117.9(4)
C(3)O(3)Mo(1)	127.3(2)	C(14)C(13)C(12)	121.2(4)
C(17)O(4)Mo(1)	134.2(3)	C(15)C(14)C(13)	119.6(4)
C(1)N(1)C(8)	115.6(4)	C(14)C(15)C(16)	121.1(5)
C(1)N(1)Mo(1)	121.9(3)	C(15)C(16)C(17)	120.0(5)
C(8)N(1)Mo(1)	122.1(3)	O(4)C(17)C(12)	121.7(4)
C(11)N(2)C(18)	115.4(4)	O(4)C(17)C(16)	118.9(4)
C(11)N(2)Mo(1)	123.9(3)	C(12)C(17)C(16)	119.4(4)
C(18)N(2)Mo(1)	120.4(3)	N(2)C(18)C(19)	113.0(4)
N(1)C(1)C(2)	125.1(4)	C(20)C(19)C(18)	124.9(5)
C(3)C(2)C(7)	118.8(4)		

Table 3. Results of physicochemical and IR spectroscopic studies for dioxomolybdenum(VI) molecular complexes and intracomplex compounds with substituted salicylidene-*N*-allylimines

Ligand	Complex	Color	T_m,°C	Bulk formula	Content (found/calcd.)			IR spectrum, cm^{-1}, for			
					Mo	N	Cl	ν(C=N)	ν(C=N)	ν(C=O)	ν(Mo=O)
HL^1	$MoO_2Cl_2 \cdot 2HL^1$	Yellow	68–69	$C_{20}H_{22}C_{l2}MoN_2O_4$	18.50/18.41		13.53/15	1630		1660	941, 902
HL^2	$MoO_2Cl_2 \cdot 2HL^2$	Orange	75–77	$C_{22}H_{26}Cl_2MoN_2O_6$	16.38/16.50		12.25/12.19	1627		1658	930, 903
HL^3	$MoO_2Cl_2 \cdot 2HL^3$	Yellow	94–96	$C_{20}H_{20}Br_2Cl_2MoN_2O_4$	14.17/14.13		10.37/10.44	1628		1657	933, 902
HL^4	$MoO_2Cl_2 \cdot 2HL^4$	Orange	88–90	$C_{20}H_{18}Br_4Cl_2MoN_2O_4$	11.42/11.46		8.35/8.47	1627		1660	932, 900
HL^5	$MoO_2Cl_2 \cdot 2HL^5$	Red	110–112	$C_{22}H_{24}Br_2Cl_2MoN_2O_6$	13.07/12.98		9.64/9.59	1627		1658	928, 904
HL^6	$MoO_2Cl_2 \cdot 2HL^6$	Brown	103–105	$C_{28}H_{26}Cl_2MoN_2O_4$	15.35/15.44		11.55/11.41	1625		1655	930, 905
HL^1	$MoO_2L^1_2$	Lemon	151–152	$C_{20}H_{20}MoN_2O_4$	21.28/21.40	6.15/6.25		1630	1624		923, 892
HL^2	$MoO_2L^2_2$	Orange	147–149	$C_{22}H_{24}MoN_2O_4$	18.80/18.86	5.37/5.51		1627	1622		920, 897
HL^3	$MoO_2L^3_2$	Yellow	156–158	$C_{20}H_{18}Br_2MoN_2O_4$	15.78/15.83	4.50/4.62		1628	1620		930, 902
HL^4	$MoO_2L^4_2$	Yellow	152–154	$C_{20}H_{16}Br_4MoN_2O_4$	12.47/12.56	3.58/3.67		1627	1618		928, 902
HL^5	$MoO_2L^5_2$	Orange	160–162	$C_{22}H_{22}Br_2MoN_2O_6$	14.58/14.40	4.16/4.21		1627	1620		930, 895
HL^6	$MoO_2L^6_2$	Yellow	154–156	$C_{28}H_{24}MoN_2O_4$	17.86/17.49	5.07/5.11		1625	1618		922, 897

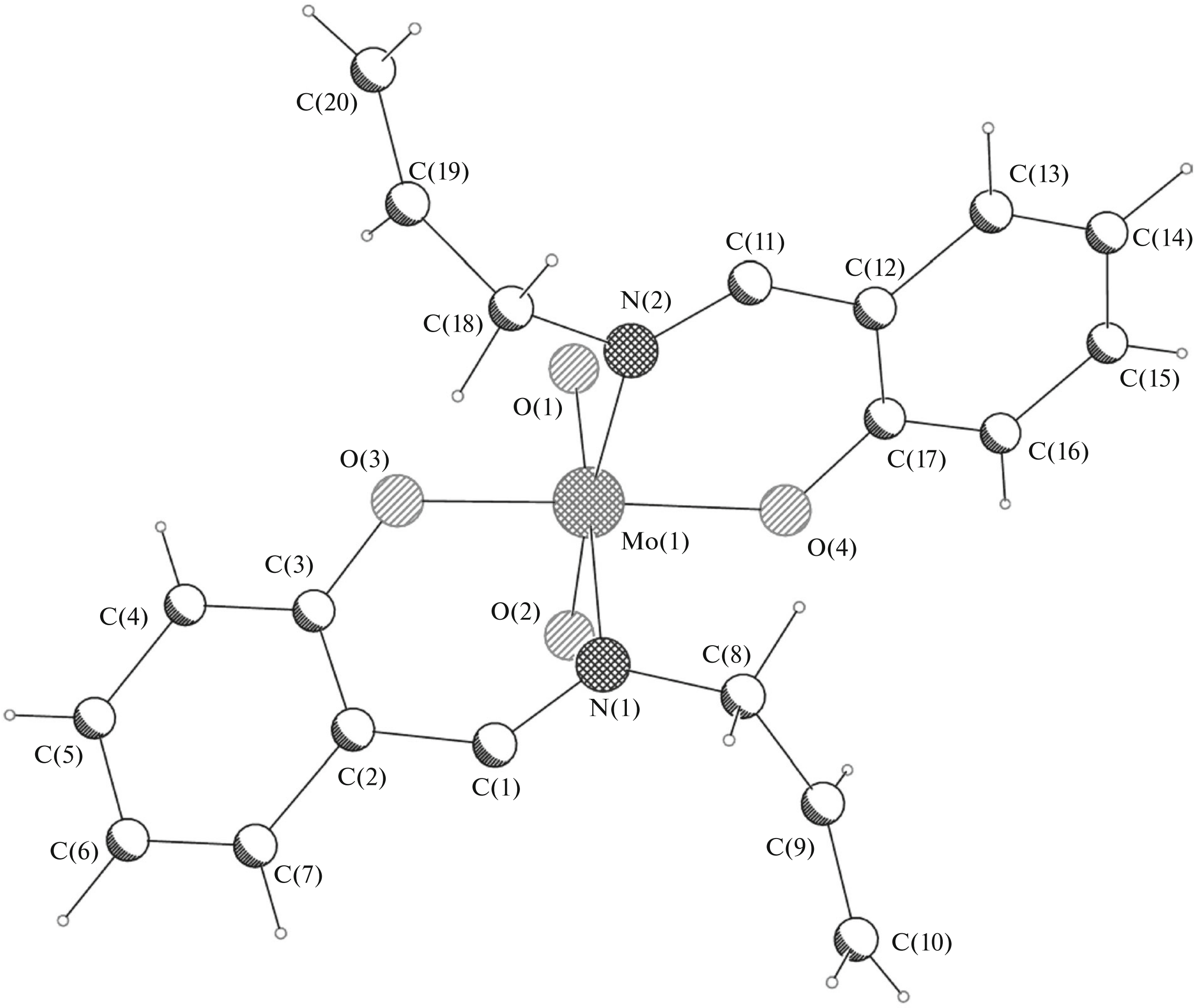
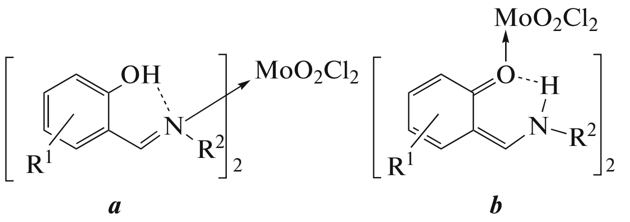


Fig. 1. Structure of complex **I**.

remains controversial. This band was considered earlier to belong to absorption by the C=N bond and should be assigned to the ν(C=N) frequency increased due to complexation by analogy with the molecular complexes of Lewis acids with benzalanilines [5], thereby implying the occurrence of the benzoid tautomeric form of *o*-oxyazomethines in the complexes $MoO_2Cl_2 \cdot 2HL^m$ (Scheme 2, structure ***a***).



Scheme 2.

However, the X-ray diffraction data obtained by now for the molecular complexes of some metals with *o*-oxyazomethines [13–18] indicate that ligands L^n are coordinated in the quinodal tautomeric form. In view of the literature data, structure ***b*** with a ligand coordinated to the molybdenum atom via the carbonyl oxygen atom of a quinodal tautomer seems to be more probable for the molecular complexes of molybdenum dioxochloride and salicylidene allylimines synthesized by us. The absorption band observed in the IR spectra at ~1650–1660 cm^{-1} is likely to belong to the decreased ν(C=O) frequency of a quinodal tautomer (***b***) instead of the frequency increased due to complexation for the stretching vibrations of the azomethine bond of a benzoid tautomer (***a***).

An intensive doublet at 950–900 cm^{-1} indicates that the multiply bonded oxygen atoms of the MoO_2^{2+} molybdenyl group are in *cis* positions. The low-frequency region of the IR spectra of these complexes contain new absorption bands, which should be assigned to the stretching vibrations of the $Mo–O_{HL}$

bond (for molecular complexes) or the Mo–N_L and Mo–O_L bonds (for intracomplex compounds) [3, 4].

Hence, based on the results of elemental analysis and IR spectroscopic studies, we may conclude that the synthesized dioxomolybdenum(VI) molecular complexes and intracomplex compound with substituted salicylidene allylimines have an octahedral structure with two oxo atoms in *cis*-position to each other. The other vertices in the octahedron of molecular complexes are occupied by the two carbonyl oxygen atoms of the quinodal tautomeric form of ligands in *trans* positions to the terminal oxo atoms in compliance with the "self-consistency" rule [19] and two chlorine atoms in *trans* positions to each other. In addition to the oxo ligands of the *cis*-MoO_2 group, the vertices of the intracomplex compound are occupied by two donating nitrogen atoms in *trans* positions to the terminal oxygen atoms and the two oxygen atoms of deprotonated hydroxo groups of salicylidene imines in *trans*-position to each other.

According to X-ray diffraction data, the molybdenum atom in complex **I** has a *cis*(O_{oxo}), *cis*(N_L), *trans*(O_L) octahedral coordination (Fig. 1). Similarly to all the other dioxo complexes of Group V–VII metals d^0-M^{5+x} (x = 0–2; M = V^{5+}, Nb^{5+}, Mo^{6+}, W^{6+}, Tc^{7+}, Re^{7+}), the O(oxo) ligands in complex **I** are in *cis* positions to each other. According to the "self-consistency" rule [19], the *trans* positions to oxo ligands are occupied by the neutral nitrogen atoms of ligands L (the bonds with which can be more easily weakened), and the *cis* positions to them are occupied by acido atoms O(L). The Mo–N bonds (avg., 2.351 ± 0.018 Å) are elongated due to the structural manifestation of the *trans* effect of the multiply bonded ligands by 0.24 Å in comparison with the standard Mo–N(ST) distance of 2.11 Å [19]. The bonds Mo–O(oxo) (avg., 1.691 ± 0.006 Å) and Mo–O(L) (avg., 1.954 ± 0.009 Å) have a standard length. The coordination of ligands L to the metal atom closes two chelate rings with different asymmetric conformations. The neighboring Mo(1) and N(1) atoms in the Mo(1)–N(1)–C(1)–C(2)–C(3)–O(3) chelate ring deviate to the same direction at 1.136 and 0.304 Å, respectively, from the plane of the four nearly coplanar (±0.003–0.063 Å) O(3) and C(1–3) atoms, while the neighboring Mo(1) and O(4) atoms in the Mo(1)–N(2)–C(11)–C(12)–C(17)–O(4) chelate ring deviate to opposite directions at –0506 and +0.148 Å, respectively from the plane of the coplanar (±0.015–0.033 Å) N(2) and C(11, 12, 17) atoms.

The structure of complex **I** has no short intermolecular contacts corresponding to hydrogen bonds.

REFERENCES

1. A. D. Garnovskii, I. S. Vasil'chenko, and D. A. Garnovskii, *Today's Aspects of Synthesis of Metal Complexes. Main Ligands and Methods* (LaPO, Rostov-on-Don, 2000) [in Russian].
2. V. L. Abramenko, A. D. Garnovskii, L. V. Surpina, and A. S. Kuzharov, Koord. Khim. **11**, 918 (1985).
3. A. B. Ilyukhin, V. S. Sergienko, and V. L. Abramenko, Zh. Neorg. Khim. **39**, 912 (1994).
4. V. L. Abramenko and V. S. Sergienko, Russ. J. Inorg. Chem. **47**, 806 (2002).
5. V. L. Abramenko, Candidate's Dissertation in Chemistry (Rostov. Gos. Univ., Rostov-on-Don, 1985).
6. K. Tsukuma, T. Kawaguchi, and T. Watanabe, Acta Crystallogr., Sect. B **31**, 2165 (1975).
7. H. A. Rudbari, M. Khorshidifard, B. Askari, et al., Polyhedron **100**, 180 (2015).
8. A. I. Busev, *The Analytical Chemistry of Molybdenum* (Izd–vo Akad. Nauk SSSR, Moscow, 1962) [in Russian].
9. V. A. Klimova, *Basic Micromethods of Organic Analysis* (Khimiya, Moscow, 1967) [in Russian].
10. G. M. Sheldrick, SHELXS-86. Programm for Solution of Crystal Structure (Univ. of Göttingen, Göttingen, 1986).
11. G. M. Sheldrick, Acta Crystallogr., Sect. A **64**, 112 (2008).
12. C. G. Percy and D. A. Thornton, J. Inorg. Nucl. Chem. **35**, 2319 (1973).
13. V. S. Sergienko, A. E. Mistryukov, V. V. Litvinov, et al., Koord. Khim. **16**, 168 (1990).
14. L. Randaccio, J. Organomet. Chem. **55**, 58 (1973).
15. J. J. Bullock, M. F. C. Ladd, D. C. Povey, and H. A. Tajmir-Riahi, Acta Crystallogr., Sect. B **35**, 2013 (1979).
16. Zhan Li-juan, Zhou Yun-shan, Zeng Xi-rui, et al., J. Chem. Crystallogr. **30**, 259 (2000).
17. M. A. Torcilli, Sh. Golquhoun, D. Doucet, and R. H. Beer, Polyhedron **21**, 697 (2002).
18. G. Pavlovic, R. Katava, M. Rajic, and R. Roje, Polyhedron **123**, 285 (2017).
19. M. A. Porai-Koshitz, Izv. Jugosl. Cent. Kristallogr. (Zagreb) **9**, 19 (1974).

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